

Source and cycling of DOC in the Gulf of Mexico: Insights from $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures

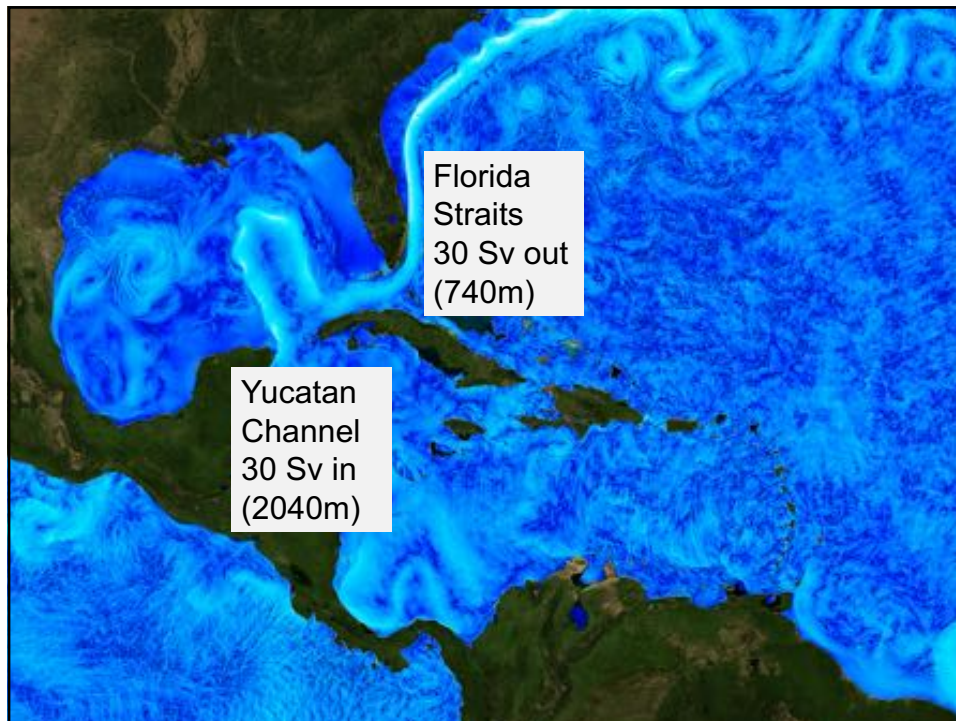
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¹University of California, Irvine

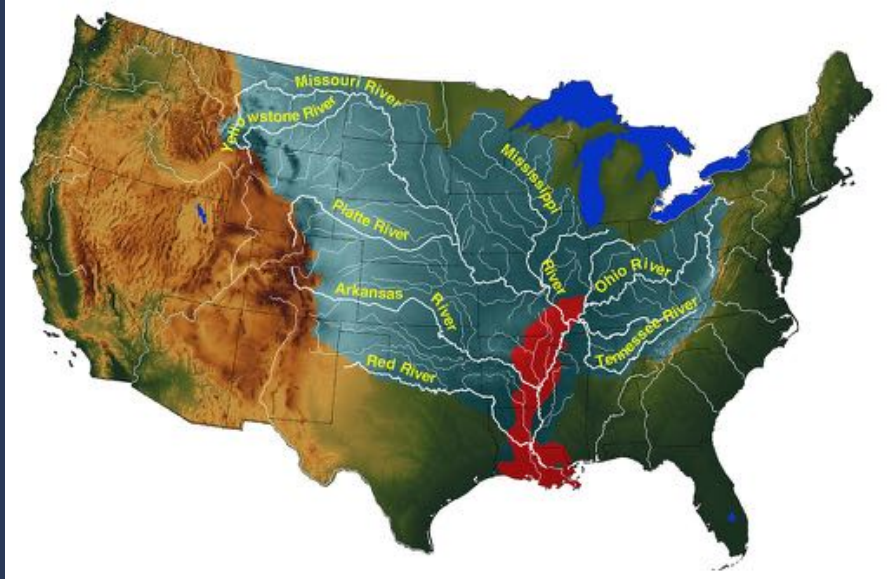
²University of South Florida

³Tulane University

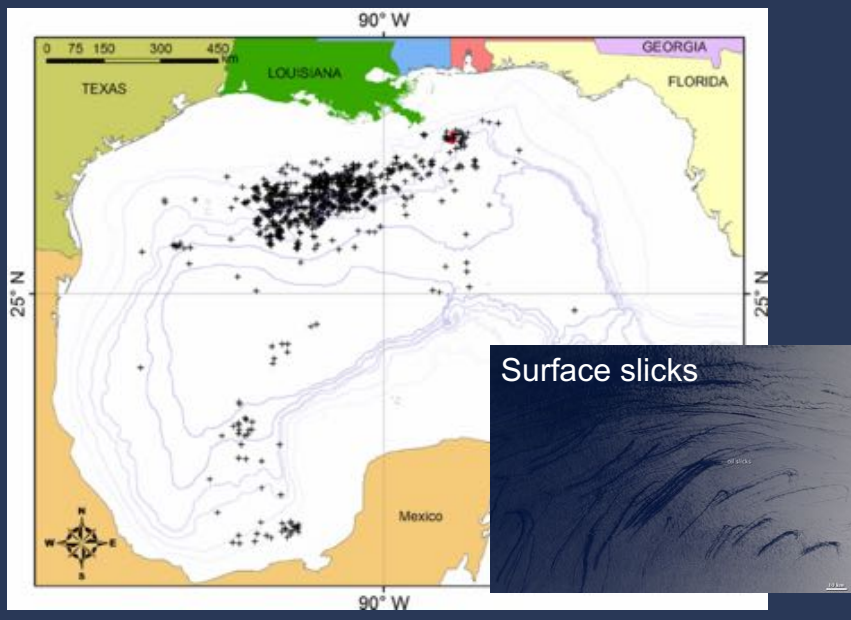
⁴Louisiana Universities Marine Consortium



Mississippi River Drainage: 3rd largest, 41% of US



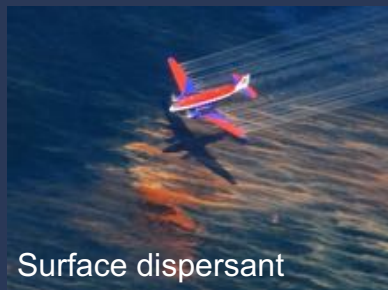
Oil in the Gulf of Mexico: natural oil seeps



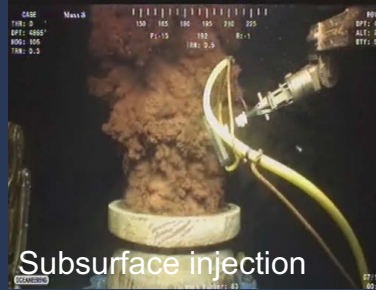
Oil in the Gulf of Mexico: Deepwater Horizon Spill



0.4-0.6 TgC

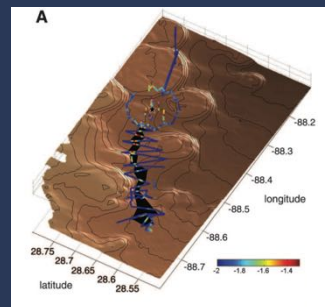
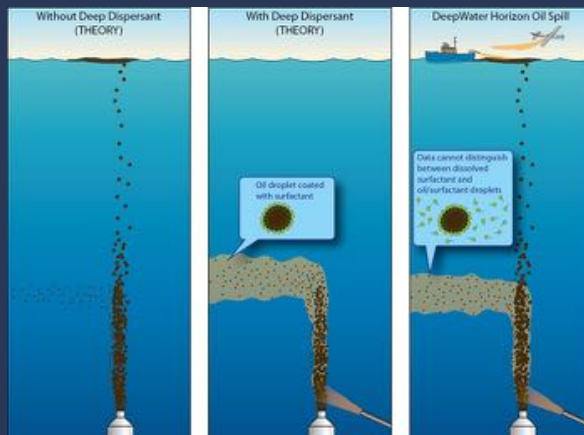


Surface dispersant



Subsurface injection

Oil in the Gulf of Mexico: Subsurface Plume



Subsurface plume mapping
(Camilli, Science 2010)

Rapid remineralization of CH_4 ,
gases, oil (~3 months)

(Kessler et al, Science, 2011)
(Valentine et al PNAS 2010)

Key Questions:



1. What is fate/cycling DOC in Mississippi R. plume?

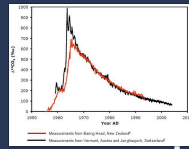
2. What are baseline DOC $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ values in Gulf of Mexico?



3. What is long-term (4 yrs) geochemical impact of DWH on DOC pool?

Carbon Isotopes: Effective Petrocarbon Tracers

Radiocarbon: $\Delta^{14}\text{C}$ (‰)



-1000‰
Geologic/
Petrocarbon

0‰
Modern

+200‰
Bomb ^{14}C

Stable carbon: $\delta^{13}\text{C}$ (‰)

-60 to -50‰
Methane

-27‰
LA Crude

-22 to -20‰
Plankton/
DOM

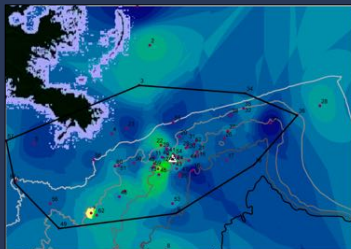
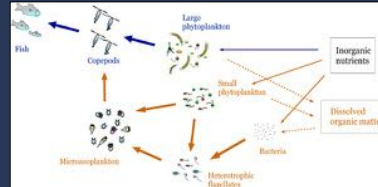
-2 to +1‰
DIC

Carbon Isotopes: Effective Petrocarbon Tracers



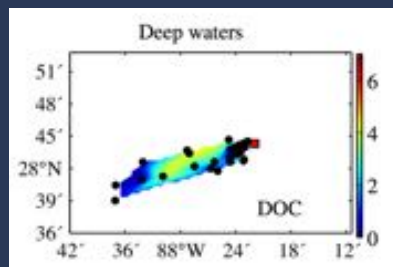
Particulate Organic Matter (POM)
(Cherrier et al, ES&T 2014)

Planktonic food web
(Chanton et al, ERL 2012)

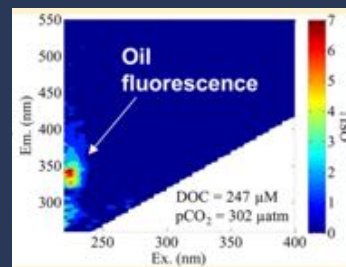


Marine Sediments
(Chanton et al, ES&T 2015)

DOC related to Deepwater Horizon



(Zhou et al, MarChem 2013)



(Bianchi et al, ES&T 2014)

Oil-like CDOM signatures, 1000-1300m depth

However, *amount* and *relative persistence* of DWH-derived DOC remains largely unconstrained

DOC Extraction for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ at UC Irvine

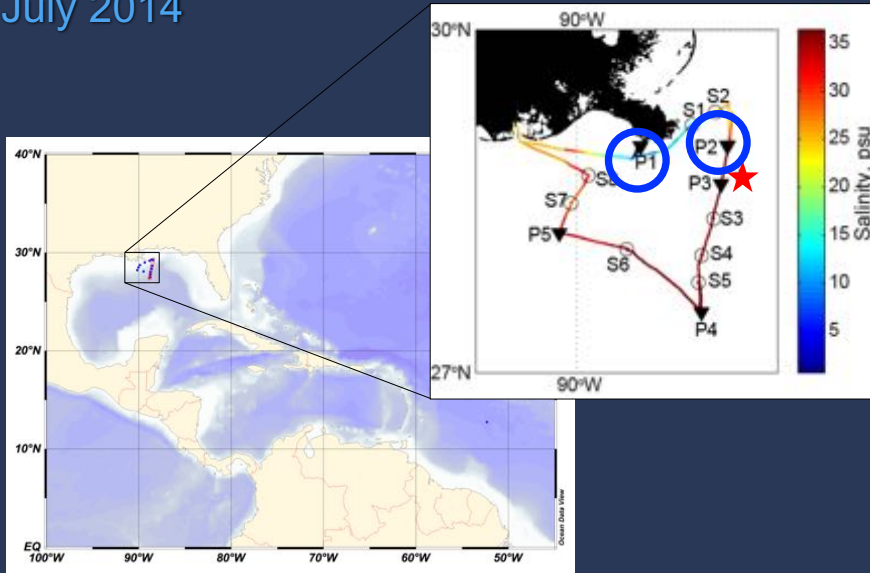


UV photo-oxidation
 $\text{DOC} \rightarrow \text{CO}_2(\text{g})$

(Beaupre et al, L&O: Methods 2007)

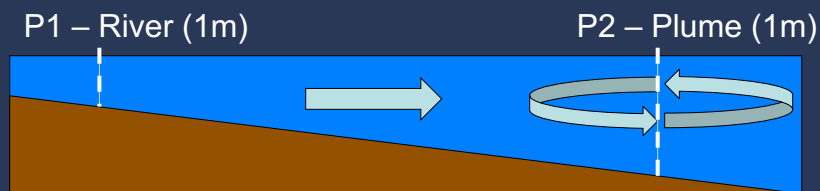
**Non-volatile DOC only
(no CH_4 , VOCs)*

CARTHE III Pelagic Cruise – PE15-01 July 2014



How is DOC cycling within
Mississippi River plume?

Large DOC + isotopic shift in river plume



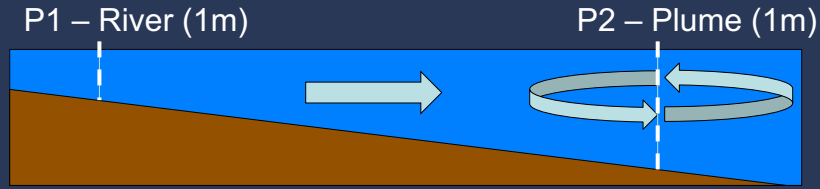
Salinity = 1.5	31.5
[DOC] = 350 μM	150 μM
$\Delta^{14}\text{C} = +5\text{‰}$	-82‰
$\delta^{13}\text{C} = -26.7\text{‰}$	-22.8‰

Mixing (salinity) P2 = 13% river water

P2 salinity predicted: [DOC] = 114 μM , $\Delta^{14}\text{C} = -184\text{‰}$

Offset suggests *modern DOC production* in plume

DOC produced has 'bomb' ^{14}C source



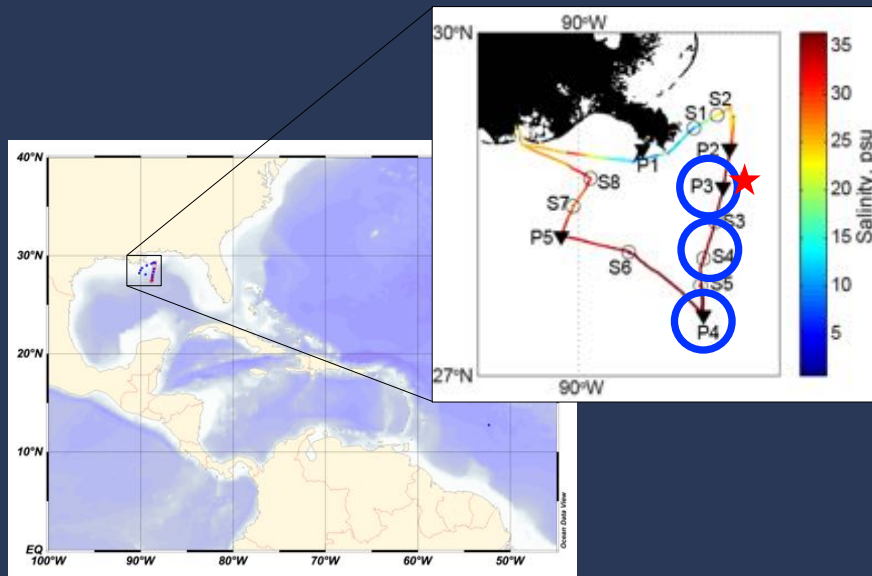
P2 observed
 DOC = 150 μM ,
 $\delta^{13}\text{C} = -22.8 \text{‰}$
 $\Delta^{14}\text{C} = -82 \text{‰}$

P2 salinity predicted
 DOC = 114 μM ,
 $\delta^{13}\text{C} = -22.7 \text{‰}$
 $\Delta^{14}\text{C} = -184 \text{‰}$

P2 isotopic mass balance
 DOC = 36 μM ,
 $\delta^{13}\text{C} = -22.8 \text{‰}$ (marine)
 $\Delta^{14}\text{C} = +218 \text{‰}$ ("bomb" ^{14}C)

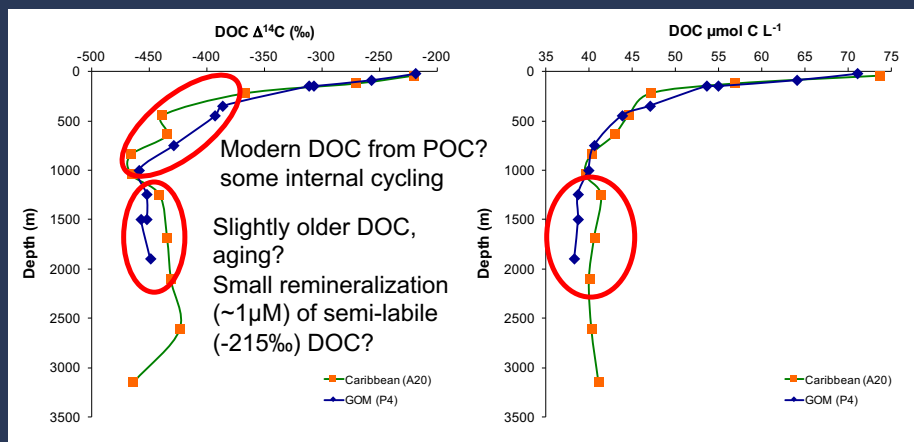
Marine DOC produced from older C source (1960's or 1980's)

Southern Abyssal Stations



What are baseline DOC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures in the GOM?

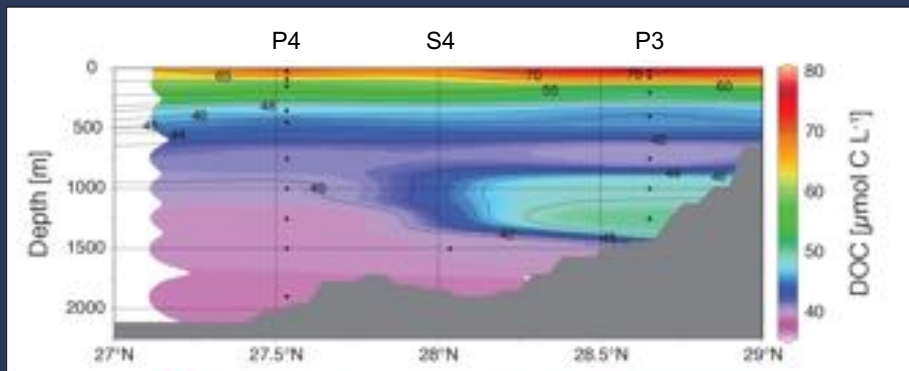
Loop Current vs. Caribbean DOC



(Walker et al, GRL 2016)

What is the long-term impact of DWH on
DOC pool 4 years after spill?

Station P3 – High [DOC] anomaly

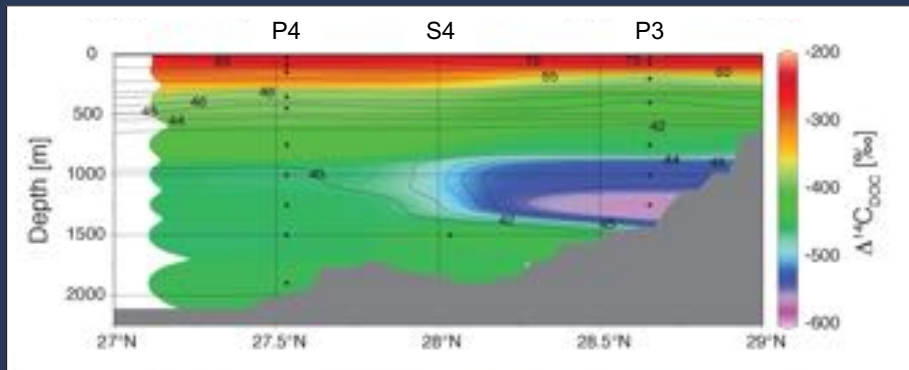


(Walker et al, GRL 2016)

Baseline Deep DOC = $39 \pm 1 \mu\text{M}$

Station P3: 1000m = 7.9 μM increase
 1250m = 9.7 μM increase

Station P3 – Negative DOC $\Delta^{14}\text{C}$ anomaly

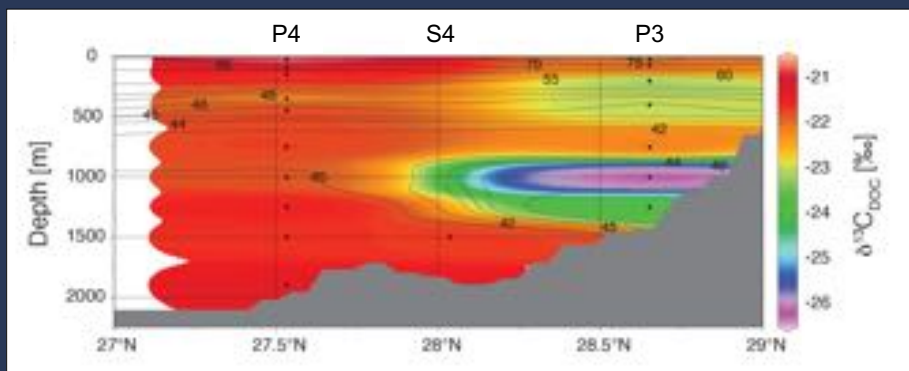


(Walker et al, GRL 2016)

Baseline Deep DOC $\Delta^{14}\text{C} = -449 \pm 11\text{‰}$

Station P3: 1000m $\Delta^{14}\text{C} = -534\text{‰}$ ($n=2$) ↓ 85‰
 1250m $\Delta^{14}\text{C} = -566\text{‰}$ ↓ 117‰

Station P3 – Negative DOC $\delta^{13}\text{C}$ anomaly

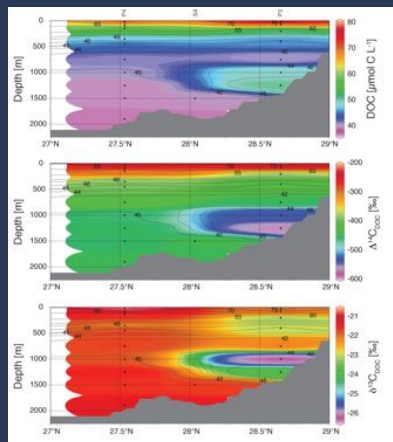


(Walker et al, GRL 2016)

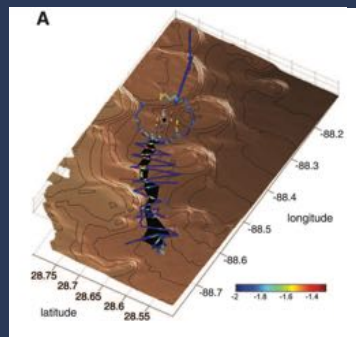
Baseline Deep DOC $\delta^{13}\text{C} = -21.6 \pm 0.2\text{‰}$

Station P3: 1000m $\delta^{13}\text{C} = -26.1\text{‰}$ ($n=2$)
 1250m $\delta^{13}\text{C} = -23.8\text{‰}$

P3 DOC anomaly consistent with deep (1000m) oil plume in 2010



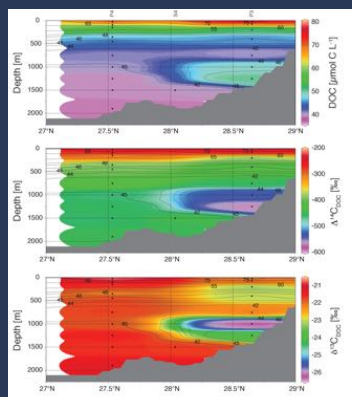
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(Camilli et al, Science 2010)

2014 plume extent = Larger (mixing/dilution)

Mass Balance: DOC anomaly = Petrocarbon



1000 - 1250m:

$\text{DOC}_{\text{pc}} = 7.9 \text{ to } 9.7 \mu\text{M}$

$\Delta^{14}\text{C} = -965 \text{ to } -1000\text{‰}$

$\delta^{13}\text{C} = -45 \pm 4\text{‰} \text{ to } -31 \pm 3\text{‰}$

$\delta^{13}\text{C}$ mass balance:

1000m DOC_{pc}

CH_4 (-60‰) vs. oil (-27‰)

58% CH_4 : 42% oil ($\pm 1\%$)

1250m DOC_{pc}

11% CH_4 : 89% oil ($\pm 2\%$)

Methanotrophic and *alkane-degrading* bacteria translated deep hydrocarbon plume into DOC

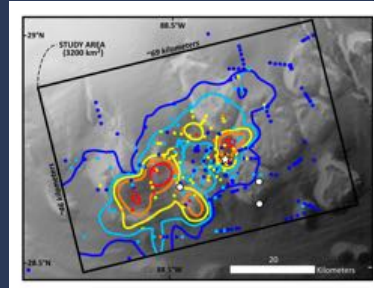
How much?

DWH Spill = 0.46 - 0.60 Tg C

DOC_{pc} = 0.061-0.075 Tg C

~10-16% of DWH spill

* likely conservative*



(Valentine et al, PNAS 2014)

Summary and Implications

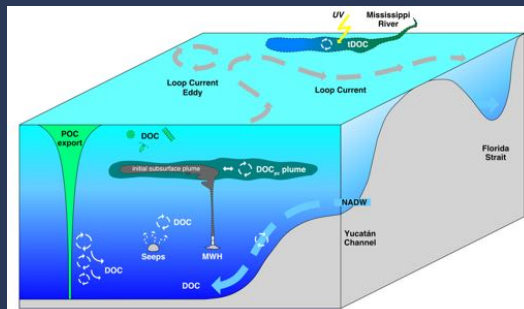
First DOC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ from GOM

River plume marine production of DOC with “bomb” ^{14}C

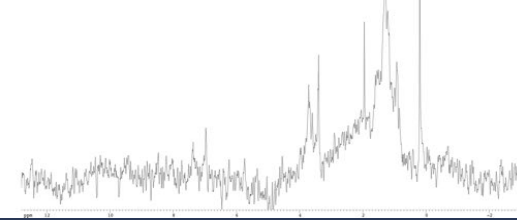
Methanotrophic and *alkane-degrading* bacteria transformed spill hydrocarbon into DOC petrocarbon

DOC_{pc} up to ~10-16% of DWH oil budget

Now persisting as a natural population of stable DOC molecules?



Total seawater $^1\text{H-NMR}$
Walker, in prep.



Thanks!

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Dachun Zhang, Jennifer Walker, Matthew Rich

Field: R/V Pelican Crew, LUMCON Staff

